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DISTRIBUTION OF CHLOROPICRIN USED ALONE OR MIXED WITH 80:20 TO FUMIGATE WHEAT AND SORGHUM

Marketing Research Report No. 894

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PRECAUTIONS

Fumigants, because of their volatility and toxicity, are hazardous when inhaled. In closed spaces these fumigants should be used only by a licensed pest-control operator or by a qualified person who is thoroughly familiar with their hazards, who will assume full responsibility for their proper use, and who knows he must comply with all precautions on the labels. Fullface masks should always be worn by persons applying fumigants in buildings or warehouses. The applicator of the fumigants is cautioned to be certain that the gas mask to be worn will provide protection against the fumigants involved. The gas mask, or the container in which it was shipped, should provide a listing of the fumigants for which protection is provided. If this information is not available for the particular mask available, a suitable mask must be obtained before applying the fumigants.

If a person is overcome by the vapor of a fumigant, prompt, on-the-spot action is essential. Carry the victim outdoors or to a room free of gas and lay him down. Remove contaminated clothing and keep him warm. Administer first-aid treatment immediately. If breathing has stopped, give artificial respiration. Call a physician immediately. Fumigators should have kits properly equipped with antidotes required for first-aid treatment of a victim of the specific fumigant being used and instructions on treatments that are to be administered only by a physician.

The maximum average atmospheric concentration (threshold limit) for each fumigant, by volume, to which workers may be exposed for an 8-hour day without injury to health, is as follows: Carbon disulfide (20 p.p.m.); carbon tetrachloride (10 p.p.m.); chloropicrin (0.1 p.p.m.). These threshold limit values were adopted at the 29th Annual Meeting of the American Conference of Governmental Industrial Hygienists, May 1967.

Carbon disulfide is flammable and explosive. Never use it near heat or open flame.

The fumigants tested here are exempt from the requirement of a tolerance for residues resulting from their use on wheat and sorghum.

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PREFACE

This report covers part of a group of tests to determine the behavior and distribution of the various components of fumigant mixtures now in common use for fumigating grain in storage. Marketing Research Report No. 897, Distribution and Retention of Fumigant Components in Shelled Corn in 3,250-bushel Metal Bins, evaluated the distribution of a 75:25 mixture of ethylene dichloride with carbon tetrachloride and an 80:20 mixture of carbon tetrachloride with carbon disulfide. This report evaluates the distribution of chloropicrin used alone or in mixture with carbon tetrachloride and carbon disulfide.

These studies were made at the Manhattan, Kans., Mid-West Grain Insects Investigations laboratory, Market Quality Research Division, Agricultural Research Service, U. S. Department of Agriculture. R. L. Ernst assisted in all of the tests. L. I. Davidson conducted the gas chromatographic analyses.

Cooperators in these fumigation studies were the Morton Chemical Company, Panogen Company Division, Woodstock, Ill.; Farmland Industries, Inc., Kansas City, Mo.; Wolf Grain Company, Bennington, Kans.; Mitchell County Cooperative, Beloit, Kans.; and the USDA storage facilities at Waterville, Frankfort, and Beloit, Kans.

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DISTRIBUTION OF CHLOROPICRIN USED ALONE OR MIXED WITH 80:20 TO FUMIGATE WHEAT AND SORGHUM

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SUMMARY

Chloropicrin concentrations and insect mortality were measured in fumigated grain to determine the distributional characteristics and effectiveness of chloropicrin used alone or mixed with carbon tetrachloride and carbon disulfide to fumigate bulk wheat and sorghum by gravity-penetration and closed-recirculation methods. Storages fumigated were 3,250-bushel bins of wheat and sorghum, 6,000-bushel bins of wheat, and a 100,000-bushel flat storage containing wheat.

In gravity-penetration fumigations with chloropicrin mixed with CCl_4:CS_2, considerable stratification of the components resulted. Chloropicrin remained in proportionately higher concentrations in the top 5 feet of grain and CCl_4:CS_2 in the bottom 5 feet.

Recirculation of the chloropicrin-CCl_4:CS_2 mixture improved the vertical distribution of the chloropicrin. The CCl_4:CS_2 part of the mixture, which had been concentrated in the bottom levels in gravity fumigations, was distributed throughout the entire grain mass. As a result, neither chloropicrin nor CCl_4:CS_2 was concentrated enough at the bottom levels to cause complete mortality of the test insects.

Even with these limitations, test insects in the wheat mass were effectively controlled with the chloropicrin-CCl_4:CS_2 mixture at dosages of 1 gallon per 1,000 bushels in gravity fumigations and 0.6 gallon per 1,000 cubic feet (¾ gallon per 1,000 bushels) in recirculation fumigations. These results compared favorably with mortality of test insects in 80:20 fumigations at dosages of 3 gallons per 1,000 bushels in gravity fumigations and 1.2 gallons per 1,000 cubic feet in recirculation fumigations.

Chloropicrin applied alone from pressurized cylinders was well suited to the recirculation method. Distribution of chloropicrin was governed by the air-movement capacity of the aeration system, although sorption loss limited distribution, particularly in sorghum fumigations.

Chloropicrin applied from cylinders pressurized with 15-percent methyl chloride was effective in closed-recirculation fumigations in 3,250-bushel bins of wheat at dosages of 1.85 pounds per 1,000 cubic feet. It gave poor results at bottom levels of the grain mass in recirculation fumigations in sorghum at dosages of 2.8 pounds per 1,000 cubic feet.

Chloropicrin recirculated from cylinders pressurized with air was effective at 2 pounds per 1,000 cubic feet in a large flat storage of wheat.

INTRODUCTION

Moore *(4)*,[1] in 1917, is generally credited with first showing the toxicity of chloropicrin as an insect fumigant. Between 1920 and 1925, many agricultural experiment station circulars and bulletins listed chloropicrin as a promising grain fumigant, but gave little information on dosages or methods of application.

Strand *(7)* in 1927 found that chloropicrin did not sink down very far in a mass of grain. He attributed this to sorption of the gases by the top layer of grain. In an early report from the U.S.S.R., Parfent'ev *(5)* discussed the practical application of chloropicrin in a large grain mass. The chloropicrin was sprayed down the wall of a grain silo and allowed to evaporate. The silo was then filled with grain "which fell through air saturated with the vapors of the insecticide." Control measures recommended for elevators in 1938 by Cotton and Wagner *(2)* included chloropicrin applied to the grain stream at the rate of 2 pounds per 1,000 bushels.

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[1] Italic numbers in parentheses refer to Literature Cited, p. 19.

Redlinger et al. *(6)* tested chloropicrin alone and mixed at the rate of 2 pounds of chloropicrin with 1 gallon of CCl_4, 80:20, or 75:25, in steel bins of shelled corn. The corn was in poor condition. Chloropicrin sprinkled over the top of the corn or raked in just below the surface was ineffective at dosages ranging from 2 to 4 pounds per 1,000 bushels. Control was also incomplete with the chloropicrin mixtures at dosages of 1 to 2 gallons per 1,000 bushels of corn.

Throughout much of its history, chloropicrin has been referred to as a tear gas, but due to its relatively low vapor pressure (23.8 mm. Hg @ 25° C. (77° F.) and 10.37 mm. Hg @ 10° C. (50° F.)) and corrosive action on metals, it has been commonly marketed in glass bottles and applied as a liquid fumigant. To facilitate handling the large amounts of chloropicrin required in flour mills and large bulk grain storages constructed during the 1950's, chloropicrin was formulated with methyl bromide or pressurized with methyl chloride in metal cylinders and discharged as a fine mist from which the chloropicrin volatilized. The development of the pressurized cylinder enabled fumigators to apply chloropicrin directly to bulk grain by the recirculation method. Cylinders that can be pressurized with air just before application have also been developed. These techniques have been used extensively, particularly in flat storages, throughout the mid-prairie States during recent years.

Although chloropicrin has been used as a grain fumigant for many years, published data on its distribution in large grain masses are nearly nonexistent. Some laboratory data by Lindgren and Vincent *(3)*, and Berck *(1)*, show the high sorption rate of chloropicrin in corn and wheat, yet little is known about what actually happens to the large amounts of chloropicrin used in commercial fumigation.

These studies were planned to determine the distributional characteristics and effectiveness of selected dosages of chloropicrin used alone or mixed with carbon tetrachloride and carbon disulfide for the fumigation of bulk wheat and sorghum. Chloropicrin concentrations throughout the entire grain mass were recorded to establish the value and limitations of chloropicrin as a grain fumigant. The gravity-penetration method was tested in 3,250-bushel metal circular bins. The closed-recirculation method was tested in 3,250-bushel bins, 6,000-bushel bins, and a large flat storage of 100,000-bushel capacity.

GRAVITY-PENETRATION TESTS

Series I—3,250-Bushel Bins

Procedure.—At the CCC binsite near Beloit, Kans., twenty 3,250-bushel circular metal bins filled with wheat were fumigated by the gravity-penetration method.

Ten bins were treated with a formulation mixed on a weight basis containing 70.7 percent carbon tetrachloride (CCl_4), 15.0 percent chloropicrin (CCl_3NO_2), 14.0 percent carbon disulfide (CS_2), and 0.3 percent inert ingredients. Each gallon of this mixture contained about 2 pounds of chloropicrin. Five bins were treated at the rate of ¾ gallon of the mixture per 1,000 bushels, and 5 bins at 1½ gallons per 1,000 bushels. For comparison, 5 bins were treated with a standard mixture of 80:20 (carbon tetrachloride 83.5 percent: carbon disulfide 16.5 percent), at a rate of 3 gallons per 1,000 bushels. This dosage is used at most CCC binsites in the routine fumigation of wheat in 3,250-bushel bins. Five bins contained control test insects but received no fumigant.

The chloropicrin-CCl_4:CS_2 mixture was applied through a rotating ring nozzle suspended above the surface of the wheat. The 80:20 was sprayed through a hand-operated nozzle onto the wheat surface from the top of the bins.

Gas concentrations within the wheat mass were sampled with a thermal conductivity (T/C) unit from 3 bundles or tiers of probes at 30 minutes, 4 hours, 8 hours, and 24 hours after application of the fumigant. Each tier of probes drew gas samples from the 2½-, 5-, 10-, and 15-foot or bottom levels. One sampling tier was placed near the north wall, a second 4 feet from the bin wall, and a third in the center of the bin.

The T/C readings, expressed as units on the galvanometer scale, indicate the total gases present, but do not differentiate between the individual components of the chloropicrin-CCl_4:CS_2 mixture. However, since the bulk of the mixture is CCl_4, which produces a strong T/C signal, the readings represent the CCl_4 distribution and indicate the comparative gas concentrations at the various sampling points.

Additional gas samples were drawn for chloropicrin analyses and bubbled through isopropyl alcohol. The scrubbed samples were submitted to the Panogen Company Division of the Morton Chemical Company, Woodstock, Ill., for final analyses.

Test insects (adult confused flour beetles, *Tribolium confusum* Jacquelin duVal, and immature rice weevils, *Sitophilus oryzae* (L.)) were placed inside a short section of perforated pipe attached to the bottom of each gas sampling probe. The confused flour beetles were held in the laboratory up to 2 weeks after the 1-week fumigation exposure period. Emergence of immature rice weevils was counted 6 weeks after exposure to the fumigant and compared to the emergence from untreated samples.

During the fumigation, the wind was about 5 m.p.h., and the temperature was in the upper seventies. Grain temperatures ranged from 64° to 90° F. in the center of the bins and from 71° to 97° F. a foot from the north wall of the bins.

Results.—Poor fumigant distribution in each of the chloropicrin-CCl_4:CS_2 fumigations was attributed to the restricted spray pattern produced by the rotating ring nozzle as it distributed the fumigant over the wheat surface. The actual effectiveness of the two dosage rates of the chloropicrin mixture was obscured due to the excessive concentrations of fumigant deposited in the center of the bins. However, insect mortality averaged higher at the 1½-gallon than at the ¾-gallon dosage, especially in the tier of probes near the wall of the bins.

The components of the chloropicrin-CCl_4:CS_2 mixture tended to separate as they settled through the wheat mass. The chloropicrin remained in proportionally higher concentrations in the top 5 feet of the wheat. The carbon tetrachloride concentrations, as indicated by the T/C readings, were highest at the bottom and 10-foot levels. Separation of the fumigant components was also reflected in the difference in mortality between the adult and immature test insects at the upper and lower levels of the wheat mass. Mortality of adult confused flour beetles was low and mortality of the immature rice weevils was fairly high at sample locations in the upper part of the grain mass. These levels contained some chloropicrin, but relatively little of the CCl_4:CS_2 components as indicated by the T/C readings. The mortality relationship was reversed at sample locations in the lower part of the grain mass, which contained only traces of chloropicrin but produced moderate T/C readings.

In the 80:20 fumigations, the fumigant was more evenly distributed over the grain surface with the hand-operated nozzle. This, together with the higher dosage rate, gave fumigant concentrations at all sample levels high enough to kill 100 percent of the adult confused flour beetles and 99 percent of the immature rice weevils. Insect mortality in the unfumigated bins was negligible.

Series II—3,250-Bushel Bins

Procedure.—Twenty more 3,250-bushel circular metal bins of wheat at the CCC binsite at Beloit, Kans. were fumigated by the gravity-penetration method in Series II.

Five bins were treated with 1 gallon of the chloropicrin-CCl_4:CS_2 mixture per 1,000 bushels of wheat. Five other bins were treated with the same mixture at 1½ gallons per 1,000 bushels. Five bins were treated with 3 gallons of 80:20 per 1,000 bushels, for comparison. The controls were 5 additional bins of wheat.

In this second series, a hand-operated nozzle was substituted for the rotating ring nozzle. It was hoped that a more uniform surface application of the fumigant would eliminate the high gas concentrations in the center of the bin as obtained with the rotating ring nozzle, and thus the effectiveness of the chloropicrin-CCl_4:CS_2 mixture could be more accurately judged. The fumigants were pumped from 5-gallon cans through a 1-inch hose and a nozzle held in the hand. The flattened nozzle produced a very coarse spray. Application in each bin took about 1 to 2 minutes.

Gas was sampled with the T/C unit from 3 tiers of probes at 3, 8, and 24 hours, and 1 week after application of the fumigant. The probes were placed at depths of 2½, 5, 10, and 15 feet. One tier was near the north wall, another was 4 feet from the wall, and one was in the center of the bin.

Chloropicrin analyses were made from each of the 10 bins treated with the chloropicrin-CCl_4:CS_2 mixture. The gas samples were drawn through a glass gas diffuser in a small bottle containing about 10 ml. of glacial acetic acid. A small rotometer measured air movement through the plastic sample lines ahead of the gas diffuser. The acetic acid samples were analyzed for chloropicrin by the Panogen Company Division.

Immature rice weevils and adult confused flour beetles were exposed at each tier of probes as in the Series I tests. In addition, 4 small screen cages, each containing 10 dermestid larvae (*Trogoderma* sp.), were placed at a depth of about 6 inches in the grain, 1 foot from the bin walls in each bin. Mortality of dermestids was determined as for the confused flour beetles.

All of the 20 fumigations took place within 3 hours. During the applications and the following 1-week exposure period, there was almost no wind. Daytime temperatures were in the upper eighties.

Grain temperature at depths of 2 to 15 feet ranged from 53° to 88° F. in the center of the bins, and from 72° to 100° F. 1 foot from the north wall of the bins.

Results.—Results of the chloropicrin analyses and test-insect mortality counts in the chloropicrin-CCl_4:CS_2 fumigations are in tables 1 and 2.

As in the Series I tests, considerably higher chloropicrin concentrations were found at the 2½- and 5-foot levels than at the 10- and 15-foot levels. The progress of the chloropicrin down through the wheat mass, as indicated by the chloropicrin concentrations at different sampling intervals, was as follows: 3 hours after application of the fumigant, the highest chloropicrin concentrations were found at the 5-foot levels, indicating fairly rapid penetration of the chloropicrin through the top part of the grain mass. During the next 5 hours, the chloropicrin concentrations at the 2½-foot levels showed a sharp reduction, while samples from the 10-foot levels showed an increase in chloropicrin. In the 24-hour gas samples, considerable chloropicrin had been lost from the 2½- and 5-foot levels, with only slight loss of chloropicrin at the 10- and 15-foot levels. One week after application of the chloropicrin-CCl_4:CS_2 mixture, the highest average chloropicrin concentrations were found at the 15-foot levels. Nearly the same amounts of chloropicrin were recorded in the 1-week samples as in the 24-hour samples at the 15-foot level.

Somewhat higher total chloropicrin concentrations were recorded in the bins treated with 1 gallon per 1,000 bushels than in the bins receiving the higher 1½-gallon per 1,000-bushel dosage. This may have been due to two or three unusually high chloropicrin concentrations recorded in the lower-dosage bins in the tier of probes 4 feet from the wall at the 2½- and 5-foot levels, rather than to an error in analyses of the chloropicrin concentrations.

Distribution of the CCl_4:CS_2 part of the mixture, as indicated by the T/C signals, differs considerably from the distribution of the chloropicrin. Three hours after application of the fumigant, the highest T/C signals were recorded at the 10-ft levels, and the lowest signals were detected at the 2½-foot levels. During the 8-hour reading, the highest signals were recorded at the 15-foot levels. The T/C signals remained highest at the 15-foot levels throughout the rest of the 1-week exposure period. Total T/C signals recorded in the bins treated at 1½ gallons per 1,000 bushels were higher than those in the bins treated at 1 gallon per 1,000 bushels.

The average T/C signals at the various levels during the 3-hour readings were reduced by more than 90 percent at each sampling level during the 1-week exposure period. The chloropicrin concentrations at the 2½- and 5-foot levels were also reduced more than 90 percent. However, only a 75-percent loss of interstitial chloropicrin con-

TABLE 1.—*Average chloropicrin concentrations and insect mortality in 5 gravity-penetration fumigations of wheat with a mixture of 80:20 and chloropicrin at 1 gallon per 1,000 bushels*

[Composition 70.7 percent carbon tetrachloride, 15 percent chloropicrin, 14 percent carbon disulfide, 0.3 percent inert ingredients. Metal 3,250-bushel bins. Exposure time 1 week]

Location and depth in grain	Chloropicrin concentrations				Mortality		
	After 3 hours	After 8 hours	After 24 hours	After 1 week	Adult confused flour beetles	Immature rice weevils	Dermestid larvae
	Oz./1,000 ft.^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Pct.*	*Pct.*	*Pct.*
North wall:							
2½ feet	4.2	5.0	4.0	0.8	100.0	100.0	------------
5 feet	4.9	4.4	3.4	.6	100.0	100.0	------------
10 feet	1.2	2.3	1.2	.6	100.0	100.0	------------
15 feet	1.2	.8	.6	.7	100.0	100.0	------------
4 feet from wall:							
2½ feet	25.7	9.7	5.4	.6	99.4	100.0	------------
5 feet	38.3	21.2	7.5	.9	100.0	100.0	------------
10 feet	9.4	9.5	3.8	.9	100.0	99.6	------------
15 feet	7.7	2.4	1.7	1.2	100.0	99.2	------------
Center:							
2½ feet	24.7	8.9	5.8	.9	100.0	100.0	------------
5 feet	16.3	17.1	9.7	1.1	100.0	100.0	------------
10 feet	4.2	7.4	7.0	1.4	100.0	100.0	------------
15 feet	1.8	2.0	2.8	1.9	100.0	100.0	------------
North wall—6 inches							100.0
East wall—6 inches							100.0
South wall—6 inches							98.0
West wall—6 inches							100.0

centrations occurred between the 3-hour and 1-week gas samples taken at the 10-foot levels. Chloropicrin at the 15-foot levels showed the lowest percent loss (37 percent). This may have been partly due to the low initial chloropicrin concentrations recorded at the 15-foot levels; however, the lower loss does indicate that the interstitial chloropicrin concentrations were less affected by leakage and sorption at the 15-foot levels.

Test-insect mortality in the bins treated with the chloropicrin-CCl_4:CS_2 mixture was excellent. Average mortalities of the test insects in the 5-bin 1-gallon series were: Adult confused flour beetles, 99.9 percent; immature rice weevils, 99.9 percent; and dermestid larvae, 99.5 percent. Average mortalities in the 5-bin 1½-gallon series were: Adult confused flour beetles, 100 percent; immature rice weevils, 100 percent; and dermestid larvae, 94.5 percent.

Average test-insect mortality in the 5 bins treated with 80:20 at the rate of 3 gallons per 1,000 bushels was: Adult confused flour beetles, 100 percent; immature rice weevils, 99.3 percent; and dermestid larvae, 89 percent. Test-insect mortality in the control bins was: Adult confused flour beetles, 1.3 percent, and dermestid larvae, 0 percent. An average of 67 rice weevils per cage emerged in the control bins.

Test-insect mortality and fumigant distribution show marked improvement over the results obtained with the rotating ring-nozzle applications in the first chloropicrin-CCl_4:CS_2 test series. Although the unusually calm wind conditions and sufficiently warm grain temperatures were important factors in the success of the chloropicrin-CCl_4:CS_2 and 80:20 fumigations, the high test insect mortality and excellent fumigant distribution in the 1-gallon chloropicrin-CCl_4:CS_2 fumigations were phenomenal.

TABLE 2.—*Average chloropicrin concentrations and insect mortality in 5 gravity-penetration fumigations of wheat with a mixture of 80:20 and chloropicrin at 1 ½ gallons per 1,000 bushels*

[Composition 70.7 percent carbon tetrachloride, 15 percent chloropicrin, 14 percent carbon disulfide, 0.3 percent inert ingredients. Metal 3,250-bushel bins. Exposure time 1 week]

Location and depth in grain	Chloropicrin concentrations				Mortality		
	After 3 hours	After 8 hours	After 24 hours	After 1 week	Adult confused flour beetles	Immature rice weevils	Dermestid larvae
	Oz./1,000 ft.^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Pct.*	*Pct.*	*Pct.*
North wall:							
2½ feet	1.6	1.9	1.7	0.7	100.0	100.0	----------
5 feet	2.7	1.8	2.0	.5	100.0	100.0	----------
10 feet	1.2	1.1	1.5	.4	100.0	100.0	----------
15 feet	.9	.9	.7	.6	100.0	100.0	----------
4 feet from wall:							
2½ feet	10.2	6.8	3.9	.6	100.0	100.0	----------
5 feet	6.0	8.7	4.7	.7	100.0	100.0	----------
10 feet	5.1	4.4	3.7	.8	100.0	100.0	----------
15 feet	.8	1.2	1.4	1.1	100.0	100.0	----------
Center:							
2½ feet	12.8	9.9	6.3	1.7	100.0	100.0	----------
5 feet	16.3	14.0	11.3	1.7	100.0	100.0	----------
10 feet	5.6	10.3	11.1	2.4	100.0	100.0	----------
15 feet	2.7	6.2	3.4	3.0	100.0	100.0	----------
North wall—6 inches							86.0
East wall—6 inches							92.0
South wall—6 inches							100.0
West wall—6 inches							100.0

CLOSED-RECIRCULATION TESTS

Series III—6,000-Bushel Bins

Procedure.—Six wheat-filled 6,000-bushel metal bins in Bennington, Kans., were fumigated by the closed-recirculation method. Three bins were treated with the chloropicrin-CCl_4:CS_2 mixture previously described, at a rate of ¾ gallon per 1,000 bushels (about 0.6 gallon per 1,000 cubic feet). Three bins were treated with 1½ gallons of 80:20 per 1,000 bushels (about 1.2 gallons per 1,000 cubic feet). A seventh bin held the test-insect controls.

The fumigants were pumped from 5-gallon cans through tubing to the top of the bins and released through a cluster of four fog nozzles into the air stream from the recirculation return duct. Each nozzle had an 0.066-inch orifice and delivered about 1 gallon per minute at the pump pressure of 65 p.s.i.

A horizontal perforated metal aeration duct about 12 inches in diameter extended along the floor from the center of each bin through the bin wall. The aeration ducts in each pair of bins were joined by a metal manifold having a single outlet. Two slide gates permitted aeration of either or both of the bins. For these tests, one slide gate was removed and the other was sealed. The eaves and access doors of each bin were sealed with pressure-sensitive paper masking tape before fumigation.

A 6-inch Buffalo fan, Model U671, powered by a 5-hp. gasoline engine, recirculated the fumigants. The intake was attached to the manifold, and the exhaust outlet was attached by flexible hose to the top of the bin. The fan was operated for 30 minutes in each fumigation. Static air pressures at the various gas-sampling positions in the grain were measured with a portable inclined manometer before the release of the fumigant.

Five tiers of sampling probes, each with gas-sample intakes and test-insect cages at the 2½-, 5-, 10-, and 15-foot levels, were in each bin. Three of the sampling tiers were in the grain mass near the bin wall. A fourth tier was halfway between the wall and center of the bin, and the fifth tier was in the center.

Gas was sampled with the T/C instrument at 30 minutes, 8 hours, 24 hours, and 1 week after application of the fumigant. Additional samples for chloropicrin analyses were taken from two of the three bins treated with the chloropicrin-CCl_4:CS_2 mixture. The same technique used in the Series II tests was used to obtain the chloropicrin samples.

Adult confused flour beetles and immature rice weevils were placed in the sampling probes in the same manner as previously described in this report.

Grain temperatures were measured in 2 of the 6,000-bushel bins. They ranged from 56° to 81.5° F. in the center of the bins and from 72° to 81.5°F. 3 feet from the wall of the bins. All 6 bins were fumigated within 5 hours on the same day. During this time, the wind was about 10 m.p.h., and the outside temperature was in the upper sixties.

Results.—Chloropicrin distribution and test-insect mortality in the chloropicrin-CCl_4:CS_2 fumigations are shown in table 3.

More than one-half of the total T/C signals and chloropicrin concentrations were recorded in the sampling 30 minutes after application. T/C signals detected after 1 week represented less than 4 percent of the total signal, and no chloropicrin was obtained in the 1-week samples.

The chloropicrin concentrations recorded at the end of the 30-minute recirculation period were highest at the 5- and 10-foot levels. Chloropicrin concentrations at the 2½- and 15-foot levels during the 30-minute readings were about one-half the amount at the 5- and 10-foot levels. Chloropicrin detected at 8 hours showed a sharp decrease in concentration at the 5-foot levels.

If the total chloropicrin recorded during the 30-minute sampling period represents 100 percent, the amount of chloropicrin found in each tier of sample probes was as follows:

Center tier of probes	73.6% of total chloropicrin
South tier of probes	12.4% of total chloropicrin
North tier of probes	5.7% of total chloropicrin
East tier of probes	4.6% of total chloropicrin
Center door tier of probes	3.7% of total chloropicrin

It is evident that much of the chloropicrin was deposited on the wheat surface directly beneath the fog nozzles, whereas the CCl_4:CS_2 part of the mixture was spread more evenly throughout the overhead space before it was pulled into the wheat mass.

Distribution of the CCl_4:CS_2 part of the fumigant, as indicated by the T/C signals, differs somewhat from the distribution of the chloropicrin. At the end of the 30-minute recirculation, about 30 percent of the total T/C signals were detected in the center tier of probes. T/C signals were fairly uniform in each of the four remaining tiers of probes.

During the 30-minute sampling period, the peak T/C signals were in the 5-foot levels, and the lowest signals were at the 15-foot levels. During the later sample periods, the peak signals were at the 15-foot levels, and the lowest signals were in the 2½-foot levels.

Although three-fourths of the total chloropicrin was concentrated in the center of the bins, the test-insect mortality was fairly high. Average mortality of the test insects in the three bins was for adult flour beetles 92.0 percent and for immature rice weevils 95.2 percent. Average test-insect mortality at the 2½-, 5-, and 10-foot levels was for adult flour beetles, 100 percent and for immature rice weevils, 98.9 percent. However, mortality at the 15-foot levels for flour beetles was 68.6 percent and for rice weevils 84.1 percent.

Distribution of the 80:20 was very similar to the distribution of the CCl_4:CS_2 part of the chloropicrin-CCl_4:CS_2 mixture. More than one-half of the total T/C signals were detected in the 30-minute sampling period. At the end of the 30-minute recirculation, about one-fourth of the T/C signals were found at each sample level. However, as in the chloropicrin-CCl_4:CS_2 fumigations, the T/C signals were highest in the center tier of probes.

Average mortality in the three bins treated with 1½ gallons of 80:20 per 1,000 bushels was for

TABLE 3.—*Average chloropicrin concentrations and insect mortality in 3 closed-recirculation fumigations of wheat with a mixture of 80:20 and chloropicrin at 3/4 gallon per 1,000 bushels*

[Composition 70.7 percent carbon tetrachloride, 15 percent chloropicrin, 14 percent carbon disulfide, 0.3 percent inert ingredients. Metal 6,000-bushel bins. Circulation time 30 minutes. Exposure time 1 week]

	Chloropicrin concentrations[1]				Mortality	
Location and depth in grain	After 30 minutes	After 8 hours	After 24 hours	After 1 week	Adult confused flour beetles	Immature rice weevils
	Oz./1,000 $ft.^3$	*Oz./1,000 $ft.^3$*	*Oz./1,000 $ft.^3$*	*Oz./1,000 $ft.^3$*	*Pct.*	*Pct.*
Center door:						
2½ feet	0.6	1.8	0.5	0	100.0	98.7
5 feet	1.8	3.8	.7	0	100.0	100.0
10 feet	1.9	1.6	.8	0	100.0	100.0
15 feet	.6	.6	.3	0	100.0	99.7
North wall:						
2½ feet	1.8	1.2	.6	0	100.0	100.0
5 feet	2.3	1.4	.6	0	100.0	98.0
10 feet	1.8	.9	.5	0	100.0	99.7
15 feet	2.2	1.0	.3	0	71.0	74.3
East wall:						
2½ feet	1.7	1.0	.4	0	100.0	97.0
5 feet	2.4	.6	.0	0	100.0	98.3
10 feet	1.8	.9	.0	0	100.0	97.3
15 feet	.5	.0	.0	0	27.7	64.0
Center:						
2½ feet	21.4	9.3	4.2	0	100.0	100.0
5 feet	33.8	17.0	7.4	0	100.0	100.0
10 feet	31.0	30.4	7.0	0	100.0	100.0
15 feet	13.6	12.6	6.1	0	100.0	100.0
South wall:						
2½ feet	8.0	3.6	1.8	0	100.0	98.7
5 feet	5.4	2.2	.6	0	100.0	98.7
10 feet	.0	1.5	.3	0	100.0	96.7
15 feet	1.6	.5	.0	0	44.3	82.7

[1] Average chloropicrin concentrations recorded in two fumigations.

adult confused flour beetles 99.3 percent and for immature rice weevils 96.1 percent. No mortality was noted in the adult confused flour beetles held in the control bin, and the average emergence of immature rice weevils was 69 weevils per cage. The overall test-insect mortality in each of the chloropicrin-CCl_4:CS_2 and 80:20 fumigations was excellent in consideration of the low dosages used.

It is interesting to compare the chloropicrin-CCl_4:CS_2 and 80:20 fumigations with respect to sample locations in which the insect mortality was less than 95 percent. In the chloropicrin-CCl_4:CS_2 bins, insects survived in the following locations: 12 locations at the 15-foot level, 2 locations at the 10-foot level, and 1 location each at the 2½- and 5-foot levels. In the 80:20 fumigations, insects survived at: 3 locations at the 15-foot level, 2 locations at the 10-foot level, 3 locations at the 5-foot level, and 7 locations at the 2½-foot level. Insect survival at the 15-foot level in the chloropicrin-CCl_4:CS_2 fumigations and at the 2½-foot level in the 80:20 fumigations was most common in the east tier of probes.

The rate of air movement produced by the aeration systems in these bins was very uneven throughout the grain mass. The highest airflows were recorded in the tier of probes directly above the aeration duct and nearest to the fan connections. In all six closed-recirculation fumigations, the average static pressure drop per foot depth of grain between the 5- and 10-foot levels was added to the distance between each tier of probes and the aeration duct, and from this the average rate of air movement for each tier of probes was estimated as follows: Probes nearest fan connections, 1/10 c.f.m. per bushel; center tier of probes, 1/25 c.f.m. per bushel; center-door tier of probes, 1/30 c.f.m. per bushel; east tier of probes and the tier of probes at the wall directly beyond the end of the aeration duct, 1/50 c.f.m. per bushel.

Regardless of the heavy concentrations in the center, only two 15-foot sample locations failed to contain concentrations of chloropicrin at some time during the 1-week sample period. However, low T/C signals were detected at the east-wall 15-foot levels in nearly all of the chloropicrin-CCl_4:CS_2 and 80:20 fumigations. The poor test-insect mortality at this level was attributed to the low fumigant concentrations in this part of the grain mass.

The reasons for the poor distribution in this part of the grain mass are not clear. However, it is suspected that the fresh air pulled by the aeration duct from the juncture of wall and floor seams diluted the fumigant concentrations near the walls. This, plus the higher rate of air movement in the center of the bin, caused the fumigant to funnel into the aeration duct, bypassing the 15-foot wall sample. If a tier of probes had been placed against the west wall, a similar situation would probably have been discovered, and the average test-insect mortality recorded in these fumigation tests would have been lower.

Recirculation of the chloropicrin-CCl_4:CS_2 mixture at a dosage of 3/4 gallon per 1,000 bushels appears to be nearly as effective as recirculation of 1½ gallons per 1,000 bushels of 80:20. The dosage of 3/4 gallon per 1,000 bushels actually amounts to about 9 pounds of chloropicrin and 3.9 gallons of the CCl_4:CS_2 mixture per 6,000-bushel bin, and the dosage of 1½ gallons per 1,000 bushels equals about 9 gallons of 80:20 per bin. On this basis, a pound of chloropicrin plus the CCl_4 and CS_2 in the formulation was not quite as effective as a gallon of 80:20, when both mixtures were recirculated.

Series IV—3,250-Bushel Bins

Procedure.—Four metal circular 3,250-bushel bins filled with wheat were used in a series of fumigations by closed recirculation. Two of these bins had 6-inch-diameter horizontal-duct systems, and two had 8-inch-diameter vertical-duct systems.

One horizontal-duct bin and one vertical-duct bin were treated with a formulation composed of 85 percent chloropicrin and 15 percent methyl chloride. The latter acts as a propellant to push the chloropicrin out of the cylinder. Each bin was treated with 8-1/3 pounds of the mixture, or about 1.85 pounds per 1,000 cubic feet. The fumigant was released into the bin through a 3-pound applicator attached to a 50-pound cylinder. Small doses of about 2½ pounds were spaced a few minutes apart until the total dosage had been applied.

The other two bins were treated with an 80:20-type formulation composed by weight of carbon tetrachloride 82.5 percent, carbon disulfide 16.5 percent, and inert ingredients 1 percent. In each bin, 6 gallons of this mixture, or about 1.3 gallons per 1,000 cubic feet, were released in one application, using a small centrifugal pump with a pressure of 70 p.s.i.

A 6-inch, Model U671, Buffalo fan was used to recirculate the fumigants. The intake of the fan was attached to the horizontal duct, and the exhaust side of the fan was attached by flexible hose to the top of the bins. The fumigant was released into the overhead bin space through a cluster of 4 fog nozzles and drawn down through the grain mass by operating the fan for 15 minutes.

In the vertical-duct fumigations, the fill hole in the top of the bins was covered with a lid equipped with two openings. One opening led directly to the overhead space above the grain surface, and the second opening was connected to the top of the vertical aeration duct which extended down through the grain mass. The intake of the fan was attached by flexible hose to the opening leading to the overhead space and the exhaust side of the fan was attached by flexible hose to the opening connected to the vertical aeration duct. The fumigant was released through fog nozzles in the overhead space above the grain. The vaporized fumigant was drawn out of the bin through the intake opening, then pushed back into the bin through the vertical duct. The fan was operated for 30 minutes.

The static pressures in the grain at the various sampling positions were measured with a portable inclined manometer. The grain mass was under negative pressure during recirculation in the horizontal-duct fumigations and under positive pressure in the vertical-duct fumigations.

Five tiers of gas-sampling probes with insect cages were located at the 2½-, 5-, 10-, and 15-foot levels in each bin. Three of the sampling tiers were near the bin wall, a fourth was halfway between the wall and the center, and the fifth tier was in the center.

Gas samples in the bins treated with 80:20 were read with the T/C unit from two of the wall tiers of probes and the center tier of probes at intervals of 30 minutes, 4 hours, 8 hours, and 24 hours after application of the fumigant.

Gas samples for chloropicrin analyses were drawn from two of the wall tiers and the center tier of probes with a small vacuum pump at a rate of about ½ liter per minute. They were scrubbed through isopropanol and returned to the fumigant manufacturer for analysis by the nitrite method.[2]

Due to the extra time required to purge the sample lines and scrub the air-gas samples, the sampling intervals used in the chloropicrin analyses varied somewhat from the sampling intervals used in the T/C analyses of the 80:20 fumigations.

Test insects were attached to the gas-sampling probes and exposed to the fumigant for 1 week in the same manner as in the previous series.

Grain temperatures were in the upper seventies throughout the wheat mass.

Results.—Chloropicrin distribution and test-insect mortality data in the chloropicrin closed-recirculation fumigations of wheat are in tables 4 and 5.

Distribution of the chloropicrin was fairly uniform in both the horizontal- and vertical-duct wheat fumigations. The fumigant concentrations decreased slowly during the initial exposure period, but were still well distributed throughout the grain after 24 hours. Mortality of both adult and immature test insects was complete.

In the 80:20 wheat fumigations, distribution of the fumigant was similar in the horizontal- and vertical-duct fumigations. However, fumigant concentrations were considerably lower in the horizontal-duct fumigation than in the vertical-duct fumigation. Review of the application procedures revealed that the total fumigant dosage applied in the horizontal-duct fumigation may have been miscalculated. Failure to fill the entire 100-foot length of the applicator hose with fumigant before beginning to measure the fumigant may have resulted in a somewhat lower total fumigant dosage than was intended. Although the 80:20 fumigant was fairly well distributed in the horizontal-duct fumigation, the concentrations were too low to kill all of the test insects.

Complete mortality of the adult test insects and 99.9-percent mortality of the immature insects was obtained in the 80:20 vertical-duct wheat fumigation. In the controls, average adult test-insect mortality was 0.6 percent, and an average of 45 immature rice weevils emerged per cage.

Series V—3,250-Bushel Bins

Procedure.—Four closed-recirculation fumigations were conducted in sorghum grain stored in 3,250-bushel metal circular bins. Two of the bins had vertical-duct aeration systems, and two had horizontal-duct systems. The 6-inch fan and the recirculation procedures used in these tests were the same as those used in the Series IV closed-recirculation fumigations in wheat, except that the fan operation time was extended to 20 minutes in the horizontal-duct fumigations.

One vertical-duct bin and one horizontal-duct bin were treated with chloropicrin pressurized with methyl chloride. Each bin was treated with 12.5 pounds of the mixture, or about 2.8 pounds per 1,000 cubic feet. The fumigant was released into the bin through a 3-pound applicator attached to a 50-pound cylinder. Small doses of about 2½ pounds were spaced a few minutes apart until the total dosage had been applied.

The other two bins were treated with an 80:20-type formulation composed by weight of carbon tetrachloride 82.5 percent, carbon disulfide 16.5 percent, and inert ingredients 1 percent. In each bin, 10 gallons of this mixture, or about 2.24 gallons per 1,000 cubic feet, were released in one application, using a small centrifugal pump with a pressure of 70 p.s.i.

The static pressure in the grain at the various sampling positions was measured with a portable inclined manometer.

Gas samples from each location in the 80:20

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[2] Feinsilver, L., and F. W. Oberst, Anal. Chem. 1953. 25, 820.

TABLE 4.—*Chloropicrin concentrations and insect mortality in a closed-recirculation fumigation of wheat with chloropicrin at a rate of 1.85 pounds per 1,000 cubic feet in a 3,250-bushel metal bin with a horizontal aeration duct*

[Cylinders pressurized with 15 percent methyl chloride. Circulation time 15 minutes. Exposure time 1 week. Approximate airflow 0.10 c.f.m. per bushel]

Location and depth in grain	Chloropicrin concentrations				Mortality	
	After 30 minutes to 1 hour	After 4 hours	After 7¾ hours	After 21⅔ hours	Adult confused flour beetles	Immature rice weevils
	Oz./1,000 ft^3	*Oz./1,000 ft^3*	*Oz./1,000 ft^3*	*Oz./1,000 ft^3*	*Pct.*	*Pct.*
East wall:						
2½ feet	0.5	3.2	2.4	2.2	100.0	100.0
5 feet	[1]	3.0	3.4	2.1	100.0	100.0
10 feet		4.2	3.4		100.0	100.0
15 feet		2.4	1.4	1.4	100.0	100.0
Center:						
2½ feet		5.9	4.0	2.2	100.0	100.0
5 feet		5.4	3.8	2.6	100.0	100.0
10 feet	6.4	5.8	3.8		100.0	100.0
15 feet	4.0	3.4	2.2	2.1	100.0	100.0
West wall:						
2½ feet	5.0	2.7	2.1	1.9	100.0	100.0
5 feet	4.6	3.7	1.6		100.0	100.0
10 feet	5.4	4.2	2.9	2.2	100.0	100.0
15 feet	4.0	3.7	2.4	1.9	100.0	100.0
North wall:						
2½ feet					100.0	100.0
5 feet					100.0	100.0
10 feet					100.0	100.0
15 feet					100.0	100.0
4 feet from north wall:						
2½ feet					100.0	100.0
5 feet					100.0	100.0
10 feet					100.0	100.0
15 feet					100.0	100.0

[1] Samples lost.

fumigations were read with the T/C unit at intervals of 1 hour, 4 hours, 8 hours, and 24 hours after application of the fumigant. Gas samples for chloropicrin analyses were taken at similar intervals from the bins treated with the chloropicrin mixture.

Two of four tiers of probes were in the grain mass near the bin walls, a third was 4 feet from the bin wall, and the fourth was in the center. Gas intakes and test insects were at the 2½, 5-, 10-, and 15-foot levels. Rice weevils and confused flour beetles were exposed to the fumigant for 1 week, and their mortality was recorded as previously described.

Grain temperatures in the sorghum averaged 73.7° F. 1 foot from the walls, 82.5° F. halfway between the wall and the center, and 79.8° F. in the center of the bins.

Results.—Chloropicrin distribution and test-insect mortality in the chloropicrin closed-recirculation sorghum fumigations are in tables 6 and 7.

Analyses of the chloropicrin distribution in the horizontal-duct fumigation indicated that the fumigant was well distributed down to the 10-foot level. However, except in the center location, gas concentrations at the 15-foot levels were about one-half of the concentrations at the 10-foot levels.

Table 5.—*Chloropicrin concentrations and insect mortality in a closed-recirculation fumigation of wheat with chloropicrin at a rate of 1.85 pounds per 1,000 cubic feet in a 3,250-bushel metal bin with a vertical aeration duct*

[Cylinders pressurized with 15 percent methyl chloride. Circulation time 30 minutes. Exposure time 1 week. Approximate airflow 0.03 c.f.m. per bushel at wall]

Location and depth in grain	Chloropicrin concentrations				Mortality	
	After 30 minutes to 1 hour	After 4⅓ hours	After 7¼ hours	After 21¾ hours	Adult confused flour beetles	Immature rice weevils
	Oz./1,000 ft.^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Pct.*	*Pct.*
East wall:						
2½ feet	4.5	2.9	2.4	1.8	100.0	100.0
5 feet	6.1	3.2	2.7	1.6	100.0	100.0
10 feet	5.8	3.2	2.6	---	100.0	100.0
15 feet	3.4	2.9	2.1	1.9	100.0	100.0
Center wall:						
2½ feet	5.1	6.9	8.5	4.2	100.0	100.0
5 feet	5.1	4.0	4.3	4.2	100.0	100.0
10 feet	5.8	4.2	4.2	---	100.0	100.0
15 feet	5.4	3.5	2.9	2.6	100.0	100.0
West wall:						
2½ feet	5.3	3.2	2.9	2.1	100.0	100.0
5 feet	5.6	3.5	2.9	---	100.0	100.0
10 feet	5.1	3.4	2.4	1.6	100.0	100.0
15 feet	5.4	2.6	2.7	1.8	100.0	100.0
North wall:						
2½ feet	---	---	---	---	100.0	100.0
5 feet	---	---	---	---	100.0	100.0
10 feet	---	---	---	---	100.0	100.0
15 feet	---	---	---	---	100.0	100.0
4 feet from north wall:						
2½ feet	---	---	---	---	100.0	100.0
5 feet	---	---	---	---	100.0	100.0
10 feet	---	---	---	---	100.0	100.0
15 feet	---	---	---	---	100.0	100.0

The low concentrations of chloropicrin at the bottom of the bin correlated closely with the low mortality at the 15-foot level. The wall tier of probes next to the bin doors had both the lowest fumigant concentration and the lowest insect mortality. In previous fumigation tests, this part of the grain mass was the most difficult area in which to control insects because of the loss of fumigant that leaked through the grain doors.

High initial gas concentrations were found in the center and 4-feet-from-the-wall tiers of probes in the chloropicrin vertical-duct fumigation. Considerably lower concentrations were detected in the two wall tiers of probes, particularly at the 10- and 15-foot levels. The low fumigant concentrations are reflected in the low test-insect mortality at these locations. It should be noted, however, that although adequate chloropicrin concentrations were registered at the 15-foot levels in the 4-foot-from-wall and center tiers of probes, there was no mortality among the test insects at these locations.

T C readings in the 80:20 horizontal-duct fumigation indicated that the fumigant was slightly concentrated in the center of the grain mass, but otherwise it was well distributed throughout the bin. Mortality of the adult test insects was complete at each sample location. A few immature rice weevils emerged at the 2½-, 5-, and 10-foot levels in the wall tiers of probes,

TABLE 6.—*Chloropicrin concentrations and insect mortality in a closed-recirculation fumigation of sorghum with chloropicrin at a rate of 2.8 pounds per 1,000 cubic feet in a 3,250-bushel metal bin with a horizontal aeration duct*

[Cylinders pressurized with 15 percent methyl chloride. Circulation time 20 minutes. Exposure time 1 week. Approximate airflow 0.12 c.f.m. per bushel]

Location and depth in grain	Chloropicrin concentrations				Mortality	
	After 1 to 1½ hours	After 4 hours	After 7½ hours	After 22 hours	Adult confused flour beetles	Immature rice weevils
	Oz./1,000 ft.^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Pct.*	*Pct.*
North wall:						
2½ feet	1.8	1.0	1.0	0.5	100.0	100.0
5 feet	2.9	1.4	1.0	.3	70.0	94.0
10 feet	2.2	1.1	1.0	.3	10.0	81.0
15 feet	1.3	.8	.6	.2	7.0	28.0
4 feet from north wall:						
2½ feet	1.6	1.8	1.3	.6	100.0	100.0
5 feet	3.5	2.4	1.9	.8	100.0	100.0
10 feet	3.7	2.4	1.9	.8	3.0	81.0
15 feet	1.9	1.1	1.1	.3	100.0	100.0
Center:						
2½ feet	3.2	2.1	2.1	1.0	100.0	100.0
5 feet	4.6	3.5	2.9	1.3	100.0	100.0
10 feet	4.2	3.0	2.2	1.1	100.0	100.0
15 feet	3.2	2.2	1.8	.6	0.0	83.0
East wall:						
2½ feet	3.7	2.6	2.1	.8	100.0	100.0
5 feet	3.7	2.9	2.4	1.0	100.0	100.0
10 feet	2.9	2.1	1.9	.6	100.0	98.0
15 feet	1.6	1.3	1.0	.3	0.0	10.0

which reduced the average mortality for immature test insects in the entire bin to 95 percent.

Gas distribution and test-insect mortality in the 80:20 vertical-duct fumigations were similar to those in the horizontal-duct fumigations. Again, the fumigant was slightly concentrated in the center of the grain mass. However, the overall fumigant distribution was sufficient to cause 100-percent mortality of the adult test insects and 99-percent mortality of the immature test insects.

Summaries of the average mortality of test insects for each of the chloropicrin and 80:20 closed-recirculation fumigations in Series IV and V are in table 8.

Although chloropicrin dosages were about 1 pound per 1,000 cubic feet higher in the sorghum fumigation than in the wheat fumigation, the average chloropicrin concentrations in the 4-hour samples were nearly twice as high in the wheat bins as in the sorghum bins. The difference was attributed principally to sorption loss, since bin construction, wind velocity during fumigation, temperature, and moisture were similar in each of the wheat and sorghum fumigations. A similar, but not so pronounced, sorption loss was noted between the wheat and sorghum vertical-duct 80:20 fumigations. Although in the sorghum fumigation the dosage was increased by about 1 gallon per 1,000 cubic feet, the average concentration measured by T C units after 4 hours was slightly lower in the sorghum bins than in the wheat bins. These data suggest that the difference in sorption by wheat or sorghum is much greater for chloropicrin than for 80:20.

The poor fumigant distribution in the chloropicrin sorghum fumigations may have been due partly to the method used in applying the fumigant. Pressure in the chloropicrin cylinder was low, as indicated by the extra time required to fill the 3-pound applicator attached to the main cylinder. The low application pressure did not propel the fumigant through the fog nozzles with

Table 7.—*Chloropicrin concentrations and insect mortality in a closed-recirculation fumigation of sorghum with chloropicrin at a rate of 2.8 pounds per 1,000 cubic feet in a 3,250-bushel metal bin with a vertical aeration duct*

[Cylinders pressurized with 15 percent methyl chloride. Circulation time 30 minutes. Exposure time 1 week. Approximate airflow 0.02 c.f.m. per bushel at wall]

Location and depth in grain	Chloropicrin concentrations				Mortality	
	After 1 to 1½ hours	After 4 hours	After 7 hours	After 22 hours	Adult confused flour beetles	Immature rice weevils
	Oz./1,000 ft.^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Oz./1,000 ft.*^{3}	*Pct.*	*Pct.*
North wall:						
2½ feet	1.8	1.6	1.3	1.1	100.0	100.0
5 feet	2.6	1.9	1.9	1.3	100.0	100.0
10 feet	1.1	1.1	1.0	.5	3.0	87.0
15 feet	1.1	.8	.6	.2	10.0	70.0
4 feet from north wall:						
2½ feet	4.8	2.7	1.9	1.4	100.0	100.0
5 feet	7.4	2.1	3.0	2.4	100.0	100.0
10 feet	8.6	3.4	3.0	1.9	100.0	100.0
15 feet	5.0	2.4	1.9	1.3	0.0	0.0
Center:						
2½ feet	5.6	3.0	<.1	1.4	100.0	100.0
5 feet	8.0	4.6	1.6	2.1	100.0	100.0
10 feet	7.8	5.3	1.9	2.1	100.0	100.0
15 feet	5.1	3.4	1.4	1.0	3.0	0.0
East wall:						
2½ feet	2.4	1.9	1.1	1.1	100.0	100.0
5 feet	1.3	1.1	.6	1.0	100.0	100.0
10 feet	.6	.6	.5	.6	100.0	100.0
15 feet	1.0	1.0	.3	.2	10.0	6.0

force enough for good surface distribution in the horizontal-duct fumigation nor for rapid volatilization of the fumigant in the vertical-duct fumigation.

Due to sorption losses, the lowest chloropicrin concentrations in the sorghum fumigations were recorded at the points fartherest from the point of application. Thus, the fumigant concentrations at the 15-foot levels in the horizontal-duct fumigation and in the wall tiers of probes in the vertical-duct fumigation were not high enough to produce a high mortality of the test insects.

It has been demonstrated in subsequent forced-distribution fumigations that the rapid loss of highly sorptive fumigants can be somewhat reduced by applying all the fumigant at once, rather than in several small dosages over a timed interval. Although this method of fumigant application may not materially improve the uniformity of the gas distribution, a sufficient charge of gas is moved through the grain mass to satisfy the high initial sorption, permitting the remaining fumigant concentrations to penetrate to a greater depth.

Series VI—100,000-Bushel Flat Storage

Procedure.—A closed-recirculation chloropicrin fumigation was conducted in a flat storage building with a total capacity of about 150,000 cubic feet of air space and containing 90,000 bushels of wheat. The wheat sloped from a depth of 20 feet next to the aeration fans to about 15 feet at the opposite end of the building. The grain beneath a tube used to fill the storage contained considerable grain dust and broken kernels and a heavy natural infestation of several species of stored-grain insects.

Two lengthwise 18-inch-diameter aeration ducts extended along the floor down the length of the building, 15 feet from the side walls. A 5-hp. fan outside the building was attached to each duct. One-foot-diameter return ducts connected the overhead space above the grain surface to the fan intakes.

Table 8.—*Average insect mortality for each application rate of chloropicrin and 80:20 in closed-recirculation fumigations of wheat and sorghum in 3,250-bushel metal bins*

[Cylinders pressurized with 15 percent methyl chloride. Exposure time 1 week]

Fumigant	Dosage per 1,000 cubic feet	Commodity	Type of aeration duct	Approximate airflow	Circulation time	Mortality	
						Adult confused flour beetles	Immature rice weevils
				C.f.m./bu.	*Min.*	*Pct.*	*Pct.*
Chloropicrin	1.85 pounds	Wheat	Horizontal	0.10	15	100.0	100.0
	1.85 pounds	Wheat	Vertical	.03 (at wall)	30	100.0	100.0
	2.8 pounds	Sorghum	Horizontal	.12	20	68.0	85.9
	2.8 pounds	Sorghum	Vertical	.02 (at wall)	30	70.4	78.9
80:20	1⅓ gallons	Wheat	Horizontal	.08	15	91.0	90.8
	1⅓ gallons	Wheat	Vertical	.02 (at wall)	30	100.0	99.9
	2¼ gallons	Sorghum	Horizontal	.13	20	100.0	95.3
	2¼ gallons	Sorghum	Vertical	.02 (at wall)	30	100.0	98.8
							Number
Controls		Wheat	None	—	—	.6	45.0 (Ave. emergence)
		Sorghum	Vertical	—	30	6.8	53.0 (Ave. emergence)

With the overhead ventilators and access doors sealed, chloropicrin was applied from air-pressurized cylinders at a rate of 2 pounds per 1,000 cubic feet, or 300 pounds for the entire building. The total amount was released in about 30 minutes. An 80-foot-long ½-inch-diameter plastic hose was suspended in the form of a giant U in the half of the building opposite the fans. Sixteen fog nozzles were attached in pairs to this hose at 10-foot intervals. Chloropicrin was supplied to the center of this hose, midway between the nozzle outlets. In addition, a single plastic tube extended down the length of the building at the roof peak. Short ¼-inch perforated copper tubes were crimped on the ends and attached at 20-foot intervals on this overhead line for nozzle outlets. The air-gas mixture was drawn from the overhead space through the return ducts, forced by the fans into the aeration ducts, and pushed up through the wheat mass. The fans were operated for 2 hours. After a 5-day exposure period, the fans were operated overnight without recirculation to evacuate the remaining gas from the building.

Air samples for gas chromatographic analysis of the chloropicrin were collected from 20 tiers of ⅛-inch probes in the wheat mass. Each tier of probes had gas-sample intakes and test-insect cages at 2½-, 5-, 10-, 15-foot, and bottom levels. Samples were taken at the end of the recirculation period and at 4 hours, 8 hours, and 24 hours after application of the fumigant. Static air pressure was measured at the various gas-sampling locations.

Mortality of confused flour beetles and immature rice weevils was determined by exposing them in the 20 tiers of probes in the wheat mass and also on the wheat surface and in the overhead space.

There was little wind during application of the fumigant and the 5-day exposure period. Grain temperatures ranged from the upper sixties to 100° F.

Results.—Results of the gas chromatographic analyses and test-insect mortality in the flat-storage fumigation are in table 9. The average amounts of chloropicrin detected during each sampling interval at each sampling level were compared. Air samples at the end of the 2-hour

TABLE 9.—*Average insect mortality and chloropicrin recorded in a closed-recirculation fumigation of wheat in a flat storage building at 2 pounds of chloropicrin per 1,000 cubic feet*

[Cylinders pressurized by air. Circulation time 2 hours. Exposure time 5 days]

Sampling level and depth in grain	Average chloropicrin recorded								Average mortality			
	At end of recirculation period		After 4 hours		After 8 hours		After 24 hours		Adult confused flour beetles		Immature rice weevils	
	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
	Oz./1,000ft.^{3}	*Oz./1,000ft.*^{3}	*Oz./1,000ft.*^{3}	*Oz./1,000ft.*^{3}	*Oz./1,000ft.*^{3}	*Oz./1,000ft.*^{3}	*Oz./1,000ft.*^{3}	*Oz./1,000ft.*^{3}	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Overhead[1]									100.0		100.0	
Surface[2]									100.0		99.5	95.5–100.0
2½ feet[2]	6.0	9.2–1.6	4.4	6.8–1.4	3.5	6.5–0.8	1.6	3.3–0.7	95.1	2.0–100.0	99.2	92.4–100.0
5 feet[2]	6.5	9.7–3.2	4.5	6.9–1.3	3.6	7.5–0.1	1.7	3.8–0.0	95.1	2.0–100.0	99.6	94.0–100.0
10 feet[2]	7.4	9.9–2.4	5.0	8.0–1.1	3.9	6.6–0.1	2.3	4.3–0.1	95.0	0.0–100.0	99.1	91.0–100.0
15 feet[2]	7.3	10.0–0.7	5.3	8.6–1.0	4.0	6.9–0.9	2.2	4.1–0.2	90.5	4.0–100.0	98.6	87.9–100.0
Bottom[3]	7.4	10.5–2.9	5.6	9.2–0.7	4.5	8.6–0.2	2.4	4.5–0.1	90.4	4.0–100.0	99.1	94.0–100.0

[1] Average of 2 locations.

[2] Average of 20 locations.

[3] Average of 10 locations.

recirculation contained 39 percent of the total chloropicrin concentrations detected during the 24-hour sampling period, 4-hour samples 28 percent, 8-hour samples 22 percent, and 24-hour samples 11 percent. Chloropicrin concentrations averaged 6.9 ounces per 1,000 cubic feet per sample location at the end of the recirculation period, 4.9 at 4 hours, 3.9 at 8 hours, and 2.0 at 24 hours. At the end of the recirculation period, distribution of chloropicrin was very uniform throughout the depth of the wheat, but less than one-fourth of that applied was left in the air spaces within the wheat. Samples at the 2½-foot levels contained 17.5 percent of the total chloropicrin detected at the end of the recirculation period, 5-foot samples 19 percent, 10-foot samples 21.5 percent, 15-foot samples 21 percent, and bottom samples 21 percent. This distribution pattern was similar for all of the sampling periods.

The average mortality in 110 sample locations was for adult confused flour beetles 94.7 percent and for immature rice weevils 99.2 percent. Mortality of the adult confused flour beetles was 100 percent in all but 6 of the 110 locations. Most of the surviving adults were in the sampling tier midway between the aeration ducts at the fan end of the building and directly beneath the vacuum tube that transferred wheat from the main elevator to the flat storage. The 15-foot sample in this tier of probes and the 15-foot sample in a similar tier at the opposite end of the building were the only ones that had less than 90-percent mortality of the immature rice weevils. No live insects were observed in samples taken from areas of natural insect infestations after fumigation.

As a basis for comparison, the 20 gas-sampling tiers were grouped according to their position in the wheat in relation to the aeration ducts. The groups consist of all the sampling tiers (1) directly above the aeration ducts, (2) in the four corners of the building in addition to those along the walls parallel to the ducts, and (3) along a line midway between the ducts. The average estimated time for a single air change, average chloropicrin concentration at the end of the recirculation period, and average test-insect mortality for each group are in table 10. The estimates of air-change times were based on the movement of air through a 1-foot-square column of wheat extending from the surface of the grain to the building floor and across to the nearest aeration duct. These estimated air-change times represent only the air movement through the longest possible air path. The shortest air-change times were at the tiers nearest the ducts (Group I) and the longest at the tiers located in the deepest parts of the wheat midway between the ducts (Group III). Within the latter group was the tier at the fan end of the building beneath the vacuum tube, in which tier most of the adult insects survived. A comparison of the range and average chloropicrin concentrations at the end of the recirculation in each group shows that the highest average and narrowest range in concentrations was in Group I, which had the most rapid air movement.

TABLE 10.—*Estimated air-change times in a closed-recirculation fumigation of wheat in a flat storage building*

[Based on static-pressure readings, average chloropicrin concentrations, and average insect mortality]

Location	Air-change time	Chloropicrin concentrations at end of recirculation period		Mortality	
		Average	Range	Adult confused flour beetles	Immature rice weevils
	Minutes	*Ounces*	*Ounces*	*Percent*	*Percent*
GROUP I					
Above ducts	6.2	8.4	4.3 – 10.5	100.0	100.0
GROUP II					
Corners and walls parallel to ducts	28.1	6.6	0.7 – 9.4	100.0	99.3
GROUP III					
Between ducts	33.3	5.6	1.6 – 9.4	79.8	98.1

CONCLUSIONS

The distributional behavior of chloropicrin mixed with $CCl_4:CS_2$ and applied by the gravity method was characterized by good penetration in the upper 5 feet of wheat, but only fair to poor at deeper levels. Penetration was nearly vertical, with no discernible lateral diffusion within the wheat mass. After initial penetration, settling was only minor, and persistence was excellent throughout 1-week exposure periods. The pattern of nearly vertical penetration and minimal lateral diffusion emphasizes the need for uniform surface coverage to obtain satisfactory distribution through the grain.

The distributional characteristics of the chloropicrin-$CCl_4:CS_2$ combination makes this mixture particularly effective in gravity-penetration fumigations. The concentration of the chloropicrin in the upper part of the grain mass offsets the deficiency of $CCl_4:CS_2$ at those levels. The low concentrations of chloropicrin in the deeper parts of the grain mass are supplemented by the $CCl_4:CS_2$ concentrations, which more readily penetrate the commodity.

Recirculation of the chloropicrin-$CCl_4:CS_2$ mixture improved the vertical distribution of the chloropicrin, but the circulation time was not long enough to pull the chloropicrin to the bottom of the bins. The $CCl_4:CS_2$ in this mixture was well distributed throughout the entire grain mass during recirculation, but at much lower concentrations than would have been collected in just the bottom levels of gravity fumigations. As a result, test insects at the bottom levels were not exposed to adequate concentrations of either chloropicrin or the $CCl_4:CS_2$ components to produce complete mortality.

Dosages of the chloropicrin-$CCl_4:CS_2$ mixture of 1 gallon per 1,000 bushels in gravity fumigations and 0.6 gallons per 1,000 cubic feet (¾ gallon per 1,000 bushels) in recirculation fumigations produced good results against test insects placed in bulk wheat. They compared favorably with dosages of 3 gallons of 80:20 per 1,000 bushels in gravity fumigations and 1.2 gallons of 80:20 per 1,000 cubic feet in recirculation fumigations.

Chloropicrin applied alone from pressurized cylinders was found to be well suited to the recirculation method. In general, the distribution of chloropicrin in recirculation fumigations was governed by the air-movement capabilities of the aeration system, although sorption loss, particularly in sorghum fumigations, influenced and limited distribution.

The chloropicrin was distributed when air movement was as low as 1/50 c.f.m. per bushel; however, increased airflow rates brought higher concentrations and more uniform distribution.

Chloropicrin was applied from cylinders pressurized with 15 percent methyl chloride in closed-recirculation fumigations. Dosages of 1.85 pounds per 1,000 cubic feet were effective in 3,250-bushel bins of wheat. Dosages of 2.8 pounds per 1,000 cubic feet gave poor results in the bottom part of a sorghum grain mass. Although a longer recirculation period might have pulled more of the chloropicrin to the bottom levels, it is evident that an increase in the dosage rate closer to the 4 pounds per 1,000 cubic feet recommended for sorghum fumigation in USDA Agriculture Handbook No. 331, Suggested Guide for the Use of Insecticides to Control Insects Affecting Crops, Livestock, Households, Stored Products, Forests, and Forest Products, would be required for satisfactory control of insects throughout the entire grain mass.

Recirculation of chloropicrin applied from cylinders pressurized with air was effective at 2 pounds per 1,000 cubic feet in a large flat storage of wheat.

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